PRANTSCHIMGIN – A NEW COUMARIN FROM THE ROOTS OF PRANGOS TSCHIMGANICA

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We have previously [1, 2] isolated from Prangos fedtschenkoi (Rgl. et Schmalh.) Korov. xanthotoxin (8-methoxypsoralen), which possesses photosensitizing activity [3].

The epigeal part of the roots of Prangos tschimganica B. Fedtsch, as the authors have observed, causes pronounced photodermatoses and enhanced pigmentation of the skin. We have therefore made a chemical investigation of the plant mentioned.

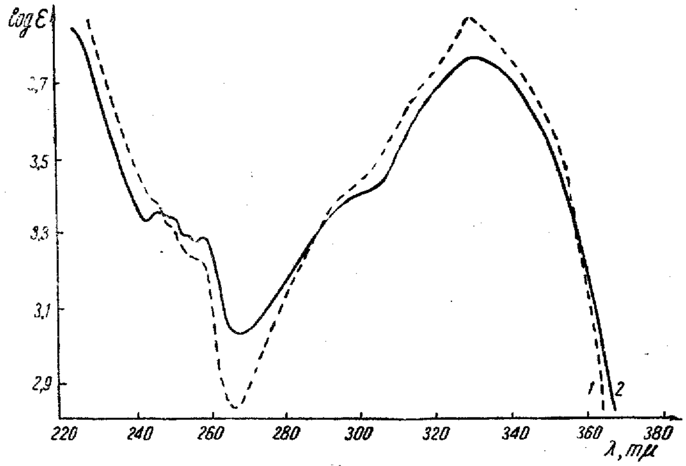


Fig. 1. UV absorption spectra of (1) prantschimgin (2) and deltoin.

Roots of P. tschimganica were collected in the region of Bol'shoi Chimgan in the Tashkent Oblast. From the results of paper chromatography, the roots of this plant contain not less than nine substances of coumarinic nature. From a concentrated alcoholic extract of the roots, we isolated three crystalline substances: A with mp 108°–109° C; B with mp 141° –142°C, and C with mp 138°–140° C. The first two substances were shown to be identical with known furocoumarins (isoimperatorin and oxypeucedanin, respectively) by their IR spectra and the absence of a depression of the melting point in admixture with authentic samples. The third substance, C, $C_{19}H_{20}O_5$, is a new coumarin, which we have called prantschimgin.

Prantschimgin exhibts properties characteristic for coumarins: with diazotized p-nitroaniline, it gives a green coloration changing to brown, and, on a paper chromatogram, it gives a spot with R_f 0.90 with a purple fluorescence under UV irradiation. The UV spectrum of prantschimgin (Fig. 1, curve 1) is similar to the spectra of 4', 5-dihydrofurocoumarins, i.e., a sharp fall in the intensity of absorption in the 240–270 mμ region and a bathochromic shift are found [4, 5]. The value of the molar absorption coefficient ($\log \varepsilon < 3.1$) in the 260–270 mμ region is very close to that for unsaturated furocoumarins and coumarins. The UV spectrum of prantschimgin [λ_{max} 254–258, 328 mμ ($\log \varepsilon$ 3.25, 3.89) and λ_{min} 268 ($\log \varepsilon$ 2.85)] is very similar to the spectrum of deltoin [λ_{max} 226, 246, 250, 258, 328 mμ ($\log \varepsilon$ 3.85, 3.35, 3.35, 3.30, 3.78) and λ_{min} 268 ($\log \varepsilon$ 3.04)] (cf. Fig. 1, curve 2).

The IR spectrum of prantschimgin (Fig. 2, a), which is very similar to the spectrum of deltoin (cf. Fig. 2, b), has absorption bands at 1712 cm^{-1} (C —O group), 1654 (aliphatic double bond), and strong bands at 1627 and 1568 (aromatic ring) and 1387 and 1364 cm^{-1} (gemdimethyl grouping). All this information permits the assumption that prantschimgin is a derivative of a 4', 5'-dihydrofurocoumarin. This is confirmed by the results of a study of the products of its degradation.

Prantschimgin [1] is readily hydrolyzed both by acids (a mixture of glacial acetic and sulfuric acids) and by alcoholic solutions of alkalies, a hydroxylactone (II) $C_{14}H_{14}O_4$ with mp 187°–188° C and an acid (III) $C_5H_8O_2$ with mp 69° C being isolated. The hydroxylactone is identical with respect to its chemical composition and IR spectrum with marmesin but in contrast to this it is optically inactive. It is evidently a racemate of two optical antipodes—marmesin and nodakenetin. Dehydration of the hydroxylactone with phosphoric acid gave a compound $C_{14}H_{12}O_3$ with mp 135° C, identical with respect to chemical composition and IR spectrum with anhydromarmesin.

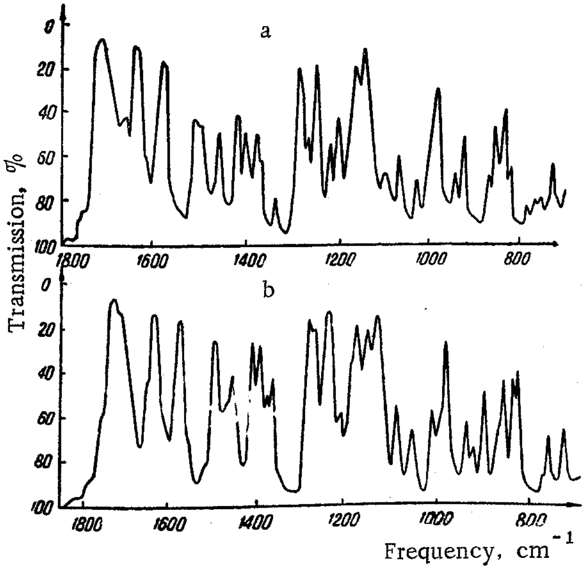
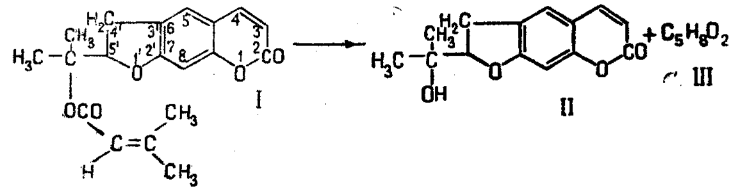


Fig. 2. IR absorption spectra of prantschimgin (a) and deltoin (b).

The acid (III) isolated from the products of the alkaline hydrolysis of prantschimgin is similar with respect to its melting point and empirical formula to 1, 2-cis-dimethylacrylic (tiglic) and 2, 2-dimethylacrylic (senecioic) acids. The anilide of this acid corresponds to the anilide of senecioic acid. The NMR spectrum of prantschimgin is also similar to that of senecioic acid.

The results mentioned permit the assumption that prantschimgin has the structure 5'-(1-senecioyloxy-1-methylethyl)-4', 5'-dihydrofuro (2', 3': 7, 6) coumarin.



Experimental

Isolation of the coumarins. 2.5 kg of the dry comminuted roots were steeped in ethyl alcohol (10 l) for 7 days. A crystalline precipitate of substance C deposited from the concentrated extract. The alcoholic extract was diluted with water (1 l) and was exhaustively extracted with ether. The ethereal extracts were combined and the ether was distilled off. The resinous residue (125 g) was transferred to a column of silica (activity grade III, 1 kg, 1 m × 4 cm). Elution was carried out with petroleum ether (fractions 1–12), and then with mixtures of petroleum ether and chloroform (4 : 1) for fractions 13–21, (3 : 2) for fractions 22–29, (2 : 3) for fractions 30–35, and pure chloroform for fractions 35–43. The volume of each fraction was 100 ml. The separation was followed by chromatographing the fractions on paper treated with a 20% aqueous solution of ethylene glycol; the mobile phase was petroleum ether (bp 60°–70° C).

Isoimperatorin. Substance A with mp 108°–109° C was isolated from fractions 13–15. The IR spectrum of this compound was identical with the spectrum of isoimperatorin. The spectrum was taken on a IKS-14 infrared spectrophotometer in paraffin oil. A mixture of substance A with isoimperatorin gave no depression of the melting point.

Found, % : C 70.84, 71.17; H 5.13, 5.32. Calculated for $C_{16}H_{14}O_4$, %: C 71.08; H 5.22.

Oxypeucedanin. Distillation of the solvent from fractions 22–24 gave crystals with mp 141–142° C. The IR spectrum of the substance coincided with that of oxypeucedanin.

Found, %: C 67.34, 67.18; H 5.02, 4.98. Calculated for $C_{16}H_{14}O_5$, %: C 67.11; H 4.93.

Prantschimgin. This was isolated from the concentrated alcoholic extract, mp 138°–140° C, $[\alpha]_D^{20}$ −23° (c 0.87; chloroform).

Found, %: C 69.76, 69.75; H 6.34, 6.53. Calculated for $C_{19}H_{20}O_5$: C 69.51; H 6.14.

Acid hydrolysis of prantschimgin. A solution of 0.12 g of prantschimgin in a mixture of 15 ml of glacial acetic acid and a few drops of sulfuric acid was left overnight. After dilution with water, the solution was extracted with ether. The concentrated ethereal extracts were separated on a column of alumina (activity grade III). Elution with a mixture of chloroform and petroleum ether (1 : 2) gave a substance with mp 187°–188° C.

Alkaline hydrolysis of prantschimgin. Two g of prantschimgin was boiled for 2 hr in the water bath with a 10% solution of potassium hydroxide in methyl alcohol. The alcohol was distilled off and the residue was dissolved in water; the solution was acidified and the crystalline precipitate that deposited was separated off and recrystallized from chloroform, after which it had mp 187°–189° C, was optically inactive, and gave no depression of the melting point with the product of acid hydrolysis. IR spectrum: 1708, 1629, 1566, 1491, 1452, 1410, 1383, 1362, 1272, 1247, 1237, 1192, 1134, 959, 880 cm^{-1}.

Found, %: C 67.90, 68.21; H 5.71, 5.92. Calculated for $C_{14}H_{14}O_4$, %: C 68.29; H 5.69;

Isolation of dimethylacrylic acid. After the hydroxylactone had been separated from the products of alkaline hydrolysis, the mother liquor was steam-distilled. The distillate was saturated with sodium chloride and extracted with ether, and the ether was distilled off. This gave dimethylacrylic acid with mp 69° C.

Preparation of 2,2-dimethylacrylanilide. A mixture of 0.2 g of dimethylacrylic acid and 1 ml of thionyl chloride was heated under reflux for 30 min. Then it was cooled, treated with 1 ml of aniline in 15 ml of benzene, and washed in a separating funnel successively with water (2 ml), 5% hydrochloric acid (2.5 ml), 5% caustic soda solution (2.5 ml), and water again (2 ml). The benzene solution was evaporated. This gave crystals with mp 126°–127° C (from petroleum ether).

Dehydration of the hydroxylactone. A solution of 0.5 g of the hydroxylactone with mp 187°–189° C in 50 ml of dry benzene was heated for 5 hr with 5 g of phosphorus pentoxide. The solution was decanted and the benzene was distilled off. The concentrated solution deposited crystals with mp 135° C having a greenish-yellow fluorescence in UV light. On a paper chromatogram it gave a spot with R_f 0.86. IR spectrum: 1728, 1645, 1595, 1580, 1463, 1382, 1292, 1193, 1071, 937, 921, 891, 881, 845, 792 cm^{-1}.

Found, %: C 74.16, 74.03; H 5.32, 5.35. Calculated for $C_{14}H_{12}O_3$, %: C 73.65; H 5.30.

The IR spectra were taken by T. V. Bukreeva, the microanalyses were carried out by E. A. Sokolova, and the NMR spectrum of prantschimgin was taken and interpreted by M. E. Perel'son. The samples of deltoin and the IR spectrum of anhydromarmesin were kindly given to us by G. K. Nikonov.

Summary

1. Isoimperatorin and oxypeucedanin have been found in the roots of Prangos tschimganica B. Fedtsch.

2. A new coumarin which we have called prantschimgin, has been isolated and its structure has been established as the ester of 5'-(2"-hydroxyisopropyl)-4',5'-dihydrofuro(2',3': 7,6) coumarin and 2,2-dimethylacrylic (senecioic) acid.

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